

09/980774

Practitioner's Docket No. U 013681-9

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PATENT TRADEMARK OFFICE

CHAPTER II

**TRANSMITTAL LETTER
TO THE UNITED STATES ELECTED OFFICE (EO/US)****(ENTRY INTO U.S. NATIONAL PHASE UNDER CHAPTER II)**

| | | |
|-------------------------------|---------------------------|-----------------------|
| PCT/RU99/00477 | 9 DECEMBER 1999 | 29 JULY 1999 |
| INTERNATIONAL APPLICATION NO. | INTERNATIONAL FILING DATE | PRIORITY DATE CLAIMED |

CATALYTIC COMPOSITION, METHOD FOR MANUFACTURING THEREOF AND METHOD FOR
THE PURIFICATION OF TEREPHTHALIC ACID

TITLE OF INVENTION

1. Anatoly Vladimirovich ROMANENKO; 2. Vladimir Alexandrovich LIKHOLOBOV;
3. Maria Nikolaevna TIMOFEEVA; 4. Jhung Sung HVA; 5. Park Jun SEOK

APPLICANT(S)

Box PCT
Assistant Commissioner for Patents
Washington D.C. 20231
ATTENTION: EO/US

CERTIFICATION UNDER 37 C.F.R. 1.10**(Express Mail label number is mandatory)**(Express Mail certification is optional)*

I hereby certify that this correspondence and the documents referred to as attached therein are being deposited with the United States Postal Service on this date OCTOBER 24, 2001, in an envelope as "Express Mail Post Office to Addressee," Mailing Label Number EV011018824US, addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231

IBIS CARRILLO

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Signature of person mailing paper

WARNING: Certificate of mailing (first class) or facsimile transmission procedures of 37 C.F.R. 1.8 cannot be used to obtain a date of mailing or transmission for this correspondence

***WARNING:** Each paper or fee filed by "Express Mail" **must** have the number of the "Express Mail" mailing label placed thereon prior to mailing 37 C.F.R. 1.10(b).
"Since the filing of correspondence under § 1.10 without the Express Mail mailing label thereon is an oversight that can be avoided by the exercise of reasonable care, requests for waiver of this requirement will **not** be granted on petition." Notice of Oct. 24, 1996, 60 Fed. Reg. 56,439, at 56,442

NOTE The completion of those filing requirements that can be made at a time later than 30 months from the priority date results from the Commissioner exercising his judgment under the authority granted under 35 USC 371(d). The filing receipt will show the actual date of receipt of the last item completing the entry into the national phase. See 37 C.F.R. §1.491 which states "An international application enters the national state when the applicant has filed the documents and fees required by 35 USC 371(c) within the periods set forth in § 1.494 and § 1.495."

WARNING: Where the items are those which can be submitted to complete the entry of the international application into the national phase are subsequent to 30 months from the priority date the application is still considered to be in the international state and if mailing procedures are utilized to obtain a date the express mail procedure of 37 C.F.R. §1.10 must be used (since international application papers are not covered by an ordinary certificate of mailing - See 37 C.F.R. §1.8

NOTE Documents and fees must be clearly identified as a submission to enter the national state under 35 USC 371 otherwise the submission will be considered as being made under 35 USC 111 37 C.F.R. § 1.494(f)

1. Applicant herewith submits to the United States Elected Office (EO/US) the following items under 35 U.S.C. 371:

- a. ☒ This express request to immediately begin national examination procedures (35 U.S.C. 371(f)).
- b. ☒ The U.S. National Fee (35 U.S.C. 371(c)(1)) and other fees (37 C.F.R. § 1.492) as indicated below:

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2. Fees

| CLAIMS FEE | (1) FOR | (2) NUMBER FILED | (3) NUMBER EXTRA | (4) RATE | (5) CALCULATIONS |
|----------------------------|--|------------------|------------------|--------------|------------------|
| <input type="checkbox"/> * | TOTAL CLAIMS | 18- 20 = | | x \$ 18.00 = | \$ |
| | INDEPENDENT CLAIMS | 1- 3 = | | x \$ 84.00 = | |
| | MULTIPLE DEPENDENT CLAIM(S) (if applicable) + \$280.00 | | | | |
| BASIC FEE** | <input type="checkbox"/> U.S. PTO WAS INTERNATIONAL PRELIMINARY EXAMINATION AUTHORITY Where an International preliminary examination fee as set forth in § 1.482 has been paid on the international application to the U.S. PTO: <input type="checkbox"/> and the international preliminary examination report states that the criteria of novelty, inventive step (non-obviousness) and industrial activity, as defined in PCT Article 33(2) to (4) have been satisfied for all the claims presented in the application entering the national stage (37 CFR 1.492(a)(4)) \$100.00 <input type="checkbox"/> and the above requirements are not met (37 CFR 1.492(a)(1)) \$710.00 <input checked="" type="checkbox"/> U.S. PTO WAS NOT INTERNATIONAL PRELIMINARY EXAMINATION AUTHORITY Where no international preliminary examination fee as set forth in § 1.482 has been paid to the U.S. PTO, and payment of an international search fee as set forth in § 1.445(a)(2) to the U.S. PTO: <input type="checkbox"/> has been paid (37 CFR 1.492(a)(2)) \$740.00 <input checked="" type="checkbox"/> has not been paid (37 CFR 1.492(a)(3)) \$1,040.00 <input type="checkbox"/> where a search report on the international application has been prepared by the European Patent Office or the Japanese Patent Office (37 CFR 1.492(a)(5)) \$860.00 | | | | |
| | Total of above Calculations | | | | =1040.00 |
| SMALL ENTITY | Reduction by ½ for filing by small entity, if applicable. Statement may also be filed. (note 37 CFR 1.9, 1.27, 1.28) | | | | - |
| | Subtotal | | | | 1040.00 |
| | Total National Fee | | | | \$1040.00 |
| | Fee for recording the enclosed assignment document \$40.00 (37 CFR 1.21(h)) (See Item 13 below) See attached "ASSIGNMENT COVER SHEET" | | | | |
| TOTAL | Total Fees enclosed | | | | \$1040.00 |

*See attached Preliminary Amendment Reducing the Number of Claims.

- i. ☒ A check in the amount of \$1040.00 to cover the above fees is enclosed.
ii. ☐ Please charge Account No. _____ in the amount of \$ _____.
A duplicate copy of this sheet is enclosed.

****WARNING.** "To avoid abandonment of the application the applicant shall furnish to the United States Patent and Trademark Office not later than the expiration of 30 months from the priority date * * * (2) the basic national fee (see § 1.492(a)) The 30-month time limit may not be extended " 37 C F R § 1.495(b)

WARNING If the translation of the international application and/or the oath or declaration have not been submitted by the applicant within thirty (30) months from the priority date, such requirements may be met within a time period set by the Office 37 C.F.R. § 1.495(b)(2). The payment of the surcharge set forth in § 1.492(e) is required as a condition for accepting the oath or declaration later than thirty (30) months after the priority date. The payment of the processing fee set forth in § 1.492(f) is required for acceptance of an English translation later than thirty (30) months after the priority date. Failure to comply with these requirements will result in abandonment of the application. The provisions of § 1.136 apply to the period which is set. Notice of Jan. 3, 1993, 1147 O.G. 29 to 40.

3. ☒ A copy of the International application as filed (35 U.S.C. 371(c)(2)):

NOTE Section 1.495 (b) was amended to require that the basic national fee and a copy of the international application must be filed with the Office by 30 months from the priority date to avoid abandonment. "The International Bureau normally provides the copy of the international application to the Office in accordance with PCT Article 20. At the same time, the International Bureau notifies applicant of the communication to the Office. In accordance with PCT Rule 47.1, that notice shall be accepted by all designated offices as conclusive evidence that the communication has duly taken place. Thus, if the applicant desires to enter the national stage, the applicant normally need only check to be sure the notice from the International Bureau has been received and then pay the basic national fee by 30 months from the priority date." Notice of Jan. 7, 1993, 1147 O.G. 29 to 40, at 35-36. See item 14c below.

- a. ☒ is transmitted herewith.
b. ☐ is not required, as the application was filed with the United States Receiving Office.
c. ☐ has been transmitted
i. ☐ by the International Bureau.
Date of mailing of the application (from form PCT/IB/308): _____
ii. ☐ by applicant on _____
Date

4. ☒ A translation of the International application into the English language (35 U.S.C. 371(c)(2)):

- a. ☒ is transmitted herewith.
b. ☐ is not required as the application was filed in English.
c. ☐ was previously transmitted by applicant on _____
Date
d. ☐ will follow.

5. ☒ Amendments to the claims of the International application under PCT Article 19 (35 U.S.C. 371(c)(3)):

NOTE The Notice of January 7, 1993 points out that 37 C F R § 1.495(a) was amended to clarify the existing and continuing practice that PCT Article 19 amendments must be submitted by 30 months from the priority date and this deadline may not be extended. The Notice further advises that "The failure to do so will not result in loss of the subject matter of the PCT Article 19 amendments. Applicant may submit that subject matter in a preliminary amendment filed under section 1 121. In many cases, filing an amendment under section 1 121 is preferable since grammatical or idiomatic errors may be corrected." 1147 O G 29-40, at 36

- a. ☐ are transmitted herewith.
b. ☐ have been transmitted
i. ☐ by the International Bureau.
Date of mailing of the amendment (from form PCT/IB/308): _____
ii. ☐ by applicant on _____
Date
c. ☒ have not been transmitted as
i. ☒ applicant chose not to make amendments under PCT Article 19.
Date of mailing of Search Report (from form PCT/ISA/210): 27 APRIL 2000.
ii. ☐ the time limit for the submission of amendments has not yet expired.
The amendments or a statement that amendments have not been made will be transmitted before the expiration of the time limit under PCT Rule 46.1.
6. ☒ A translation of the amendments to the claims under PCT Article 19 (38 U.S.C. 371(c)(3)):
a. ☐ is transmitted herewith.
b. ☐ is not required as the amendments were made in the English language.
c. ☒ has not been transmitted for reasons indicated at point 5(c) above.
7. ☒ A copy of the international examination report (PCT/IPEA/409)
☒ is transmitted herewith.
☐ is not required as the application was filed with the United States Receiving Office.
8. ☐ Annex(es) to the international preliminary examination report
a. ☐ is/are transmitted herewith.
b. ☐ is/are not required as the application was filed with the United States Receiving Office.
9. ☐ A translation of the annexes to the international preliminary examination report
a. ☐ is transmitted herewith.
b. ☐ is not required as the annexes are in the English language.

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10. ☒ An oath or declaration of the inventor (35 U.S.C. 371(c)(4)) complying with 35 U.S.C. 115
- a. ☐ was previously submitted by applicant on _____.
Date
- b. ☒ is submitted herewith, and such oath or declaration
- i. ☐ is attached to the application.
- ii. ☒ identifies the application and any amendments under PCT Article 19 that were transmitted as stated in points 3(b) or 3(c) and 5(b); and states that they were reviewed by the inventor as required by 37 C.F.R. 1.70.
- c. ☐ will follow.

Other document(s) or information included:

11. ☒ An International Search Report (PCT/ISA/210) or Déclaration under PCT Article 17(2)(a):
- a. ☒ is transmitted herewith.
- b. ☐ has been transmitted by the International Bureau.
Date of mailing (from form PCT/IB/308): _____.
- c. ☐ is not required, as the application was searched by the United States International Searching Authority.
- d. ☐ will be transmitted promptly upon request.
- e. ☐ has been submitted by applicant on _____.
Date
12. ☒ An Information Disclosure Statement under 37 C.F.R. 1.97 and 1.98:
- a. ☒ is transmitted herewith.
Also transmitted herewith is/are:
☒ Form PTO-1449 (PTO/SB/08A and 08B).
☒ Copies of citations listed.
- b. ☐ will be transmitted within THREE MONTHS of the date of submission of requirements under 35 U.S.C. 371(c).
- c. ☐ was previously submitted by applicant on _____.
Date
13. ☒ An assignment document is transmitted herewith for recording.

A separate ☒ "COVER SHEET FOR ASSIGNMENT (DOCUMENT) ACCOMPANYING NEW PATENT APPLICATION" or ☐ FORM PTO 1595 is also attached.

INSTITUT KATALIZA IMENI G.K. BORESKOVA SIBIRSKOGO
OTDELENIYA ROSSIISKOI AKADEMII NAUK and
SAMSUNG GENERAL CHEMICALS CO., LTD

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14. ☒ Additional documents:
- a. ☒ Copy of request (PCT/RO/101)
- b. ☒ International Publication No. WO 01/08798
- i. ☐ Specification, claims and drawing
- ii. ☒ Front page only
- c. ☒ Preliminary amendment (37 C.F.R. § 1.121)
- d. ☒ Other

FORM PCT/IB/304; FORM PCT/IPEA/401:

CERTIFIED COPY OF RU 99116348 WITH ENGLISH TRANSLATION

15. ☒ The above checked items are being transmitted
- a. ☒ before 30 months from any claimed priority date.
- b. ☐ after 30 months.
16. ☐ Certain requirements under 35 U.S.C. 371 were previously submitted by the applicant on _____, namely:
- _____
- _____
- _____

AUTHORIZATION TO CHARGE ADDITIONAL FEES

WARNING: Accurately count claims, especially multiple dependent claims, to avoid unexpected high charges if extra claims are authorized.

NOTE: "A written request may be submitted in an application that is an authorization to treat any concurrent or future reply, requiring a petition for an extension of time under this paragraph for its timely submission, as incorporating a petition for extension of time for the appropriate length of time. An authorization to charge all required fees, fees under § 1.17, or all required extension of time fees will be treated as a constructive petition for an extension of time in any concurrent or future reply requiring a petition for an extension of time under this paragraph for its timely submission. Submission of the fee set forth in § 1.17(a) will also be treated as a constructive petition for an extension of time in any concurrent reply requiring a petition for an extension of time under this paragraph for its timely submission." 37 C.F.R. § 1.136(a)(3)

NOTE: "Amounts of twenty-five dollars or less will not be returned unless specifically requested within a reasonable time, nor will the payer be notified of such amounts, amounts over twenty-five dollars may be returned by check or, if requested, by credit to a deposit account." 37 C.F.R. § 1.26(a)

☒ The Commissioner is hereby authorized to charge the following additional fees that may be required by this paper and during the entire pendency of this application to Account No. 12-0425.

☒ 37 C.F.R. 1.492(a)(1), (2), (3), and (4) (filing fees)

WARNING: Because failure to pay the national fee within 30 months without extension (37 C.F.R. § 1.495(b)(2)) results in abandonment of the application, it would be best to always check the above box

☐ 37 C.F.R. 1.492(b), (c) and (d) (presentation of extra claims)

NOTE: Because additional fees for excess or multiple dependent claims not paid on filing or on later presentation must

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only be paid or these claims cancelled by amendment prior to the expiration of the time period set for response by the PTO in any notice of fee deficiency (37 C.F.R. § 1.492(d)), it might be best not to authorize the PTO to charge additional claim fees, except possible when dealing with amendments after final action.

- ☒ 37 C.F.R. 1.17 (application processing fees)
- ☒ 37 C.F.R. 1.17(a)(1)-(5)(extension fees pursuant to § 1.136(a).
- ☒ 37 C.F.R. 1.18 (issue fee at or before mailing of Notice of Allowance, pursuant to 37 C.F.R. 1.311(b))

NOTE Where an authorization to charge the issue fee to a deposit account has been filed before the mailing of a Notice of Allowance, the issue fee will be automatically charged to the deposit account at the time of mailing the notice of allowance 37 C.F.R. § 1.311(b)

NOTE 37 C.F.R. 1.28(b) requires "Notification of any change in loss of entitlement to small entity status must be filed in the application prior to paying, or at the time of paying issue fee." From the wording of 37 C.F.R. § 1.28(b) (a) notification of change of status must be made even if the fee is paid as "other than a small entity" and (b) no notification is required if the change is to another small entity

- ☐ 37 C.F.R. § 1.492(e) and (f) (surcharge fees for filing the declaration and/or filing an English translation of an International Application later than 30 months after the priority date).


SIGNATURE OF PRACTITIONER

William R. Evans
(type or print name of practitioner)

Reg. No.: 25,858

Tel. No.: (212) 708-1930

Customer No.: 00140

P O Address

c/o Ladas & Parry
26 West 61st Street
New York, N.Y. 10023

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Practitioner's Docket No. U 013681-9

CHAPTER II

IN THE UNITED STATES ELECTED OFFICE (EO/US)

| | | |
|---|---------------------------|-----------------------|
| PCT/RU99/00477 | 9 DECEMBER 1999 | 29 JULY 1999 |
| INTERNATIONAL APPLICATION NO. | INTERNATIONAL FILING DATE | PRIORITY DATE CLAIMED |
| CATALYTIC COMPOSITION, METHOD FOR MANUFACTURING THEREOF AND METHOD FOR THE PURIFICATION OF TEREPHTHALIC ACID | | |
| TITLE OF INVENTION | | |
| 1. Anatoly Vladimirovich ROMANENKO; 2. Vladimir Alexandrovich LIKHOLOBOV; 3. Maria Nikolaevna TIMOFEEVA; 4. Jhung Sung HVA; 5. Park Jun SEOK | | |
| APPLICANT(S) | | |

Box PCT
Assistant Commissioner for Patents
Washington, D.C. 20231
ATTENTION: EO/US

PRELIMINARY AMENDMENT

Please amend the above identified application as follows:

IN THE CLAIMS :

Please cancel claims 1-18.

Please add the following new claims 19-36:

CERTIFICATE UNDER 37 1.10

I hereby certify that this paper is being deposited with the United States Postal Service on this date OCTOBER 24, 2001 in an envelope as "EXPRESS MAIL POST OFFICE TO ADDRESSEE" Mailing Label Number EV011018824US addressed to the: Assistant Commissioner for Patents, Washington, D.C. 20231

IBIS CARRILLO

(Type or print name of person mailing paper)

IBIS Carrillo

(Signature of person mailing paper)

NOTE: Each paper or fee referred to as enclosed herein has the number of the "EXPRESS MAIL" mailing label place thereon prior to mailing 37 CFR 1.16(b).

19. A catalyst composition for the purification of terephthalic acid from p-carboxybenzaldehyde comprising crystallites of catalytically active palladium or palladium and at least one metal of Group VIII of the Periodic Table of Elements, applied to the surface of a carbon material, wherein a mesoporous graphite-like material with the average mesopore size in the range of from 40 to 400 Å, the proportion of the mesopores in the total pore volume of at least 0.5, and the degree of graphite-similarity of at least 20% is used as the carbon material, in which metal crystallites are distributed in the volume of the carbon material granules in such a manner that the distribution peaks of these crystallites should be at a distance from the outer surface of the granule corresponding to 1-30% of its radius.

20. The catalyst composition of claim 19, wherein it comprises crystallites of rhodium and palladium.

21. The catalyst composition of claim 19, wherein it comprises crystallites of palladium and ruthenium.

22. The catalyst composition of claim 19, wherein it comprises crystallites of palladium and platinum.

23. The catalyst composition of claim 19, wherein the total content of metals therein varies within the range of from 0.1 to 3.0 percent by weight.

24. The catalyst composition of claim 19, wherein the weight ratio of palladium to other metals varies within the range of from 0.1 to 10.0.

25. A method of preparing a catalyst composition for the purification of terephthalic acid from p-carboxybenzaldehyde, claimed in claim 19, comprising in applying catalytically active palladium or palladium and at least one of Group VIII metals to the surface of granules of a carbon carrier, said granules being contacted with an aqueous solution of palladium salts or palladium salts and salts of at least one of Group VIII metals to produce a "metal salt - porous carbon" precursor, wherein the precursor is dried and treated with a reducing agent in an amount sufficient for reducing the surface metal salts to the metal crystallites, characterized in that a mesoporous graphite-like material with the average

mesopore size in the range of from 40 to 400 Å, the proportion of the mesopores in the total pore volume of at least 0.5, and the degree of graphite-similarity of at least 20% is used as the carbon material to produce a metallic or bimetallic catalyst.

26. The method of claim 25, wherein said catalyst composition is prepared, using one of the following metal precursors:

H_2PdCl_4 or $\text{Pd}(\text{NO}_3)_2$;

H_2PdCl_4 and RuOHCl_3 or $\text{RuNO}(\text{NO}_3)_3$;

$\text{Pd}(\text{NO}_3)_2$ and RuOHCl_3 or $\text{RuNO}(\text{NO}_3)_3$.

27. The method of claim 25, wherein said catalyst composition is prepared, using nitric acid solutions of palladium and/or ruthenium salts with the concentration of free nitric acid ranging from 37 to 170 g/l.

28. The method of claim 25, wherein bimetallic catalysts are prepared by combined application of metal precursors.

29. The method of claim 25, wherein bimetallic catalysts are prepared by successive application of metal precursors.

30. A method of purifying terephthalic acid from p-carboxy-benzaldehyde in the presence of hydrogen with the use of a catalyst composition claimed in claim 19, which comprises crystallites of catalytically active palladium or of palladium and at least one metal of Group VIII of the Periodic Table of Elements, applied to the surface of carbon material, characterized in that in the catalyst composition a mesoporous graphite-like material with the average mesopore size in the range of from 40 to 400 Å, the proportion of the mesopores in the total pore volume of at least 0.5, and the degree of graphite-similarity of at least 20% is used as the carbon material, wherein the metal crystallites are distributed within the volume

of granules of the carbon material in such a manner that peaks of the distribution of active components should be should be at a distance from the outer surface of the granule corresponding to 1-30% of its radius.

31. The method of claim 30, wherein the catalyst composition comprises crystallites of palladium and rhodium.

32. The method of claim 30, wherein the catalyst composition comprises crystallites of palladium and ruthenium.

33. The method of claim 30, wherein the catalyst composition comprises crystallites of palladium and platinum.

34. The method of claim 30, wherein the total content of metals in the catalyst composition varies within the range of from 0.1 to 3.0 percent by weight.

35. The method of claim 30, wherein the weight ratio of palladium to other metals in the catalyst composition varies i within the range of 0.1 to 10.0.

36. The method of claim 30, wherein the concentration of p-carboxybenzaldehydein terephthalic acid to be purified varies from 1000 to 30000 ppm.

IN THE ABSTRACT

Please substitute the Abstract on the last, separate page hereof.

Respectfully submitted,



WILLIAM R. EVANS
LADAS & PARRY
26 WEST 61ST STREET
NEW YORK, NEW YORK 10023
REG.NO.25,858 (212)708-1930

Abstract of the Disclosure

The present invention relates to catalyst compositions for purifying terephthalic acid from p-carboxybenzaldehyde, based on Group VIII metals, comprising crystallites of catalytically active palladium or of palladium and at least one metal of Group VIII of the Periodic Table of Elements, applied to the surface of a carbon material, wherein a mesoporous graphite-like material with the average mesopore size in the range of from 40 to 400 Å, the proportion of the mesopores in the total pore volume of at least 0.5, and the degree of graphite-similarity of at least 20% is used as the carbon material, in which metal crystallites are distributed in the volume of the carbon material granules in such a manner that the distribution peaks of these crystallites should be at a distance from the outer surface of the granule corresponding to 1-30% of its radius. The present invention also relates to a method for preparing catalyst compositions, and to a method of purifying terephthalic acid suitable for the subsequent synthesis of polyester polymers and copolymers used in the manufacture of textile fibers.

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Catalyst Composition, Method for Preparing thereof, 24 OCT 2001
and Method for Purifying Terephthalic Acid

Background of the Invention

5 The present invention relates to catalyst compositions for purifying terephthalic acid, based on Group VIII metals, to methods for preparing thereof, and to a method of purifying terephthalic acid suitable for the subsequent synthesis of polyester polymers and copolymers used in the manufacture of
10 textile fibers.

It is of importance that terephthalic acid which is used as a monomer in the manufacture of polymer fibers should have a high purity. The main controllable quality parameters of pure terephthalic acid are the content of p-
15 carboxybenzaldehyde and colored impurities in it.

Purified terephthalic acid is derived from less pure, technical grade or "crude" terephthalic acid by hydrofining the latter (treating in the presence of hydrogen) over Group VIII metal catalysts. Crude terephthalic acid is dissolved in
20 water at an elevated temperature, and the resulting solution is hydrogenated in a vibrated reactor or in a reactor with a stationary bed, preferably in the presence of Group VIII metal catalysts. The methods of purification, composition of the catalysts, and processes for preparing these catalysts are
25 described in numerous patents.

Description of the Related Art

The activity and selectivity of catalysts for the hydrofining of terephthalic acid depend on a great number of factors, such as the content of Group VIII metal(s) in the
30 catalyst, the type of support, the method of applying Group VIII metal(s) to the support, and also on the distribution of the metal or metals of Group VIII were applied to a support, and also on the distribution of said metal(s) over the granule of the carrier.

Known in the art is a method of hydrofining terephthalic acid [UK Patent No. 994769, 1965], wherein a palladium-on-active carbon catalyst composition displays high activity in the reaction of purifying terephthalic acid from p-carboxybenzaldehyde impurities. As supports for palladium other compounds, such as SiO_2 , Al_2O_3 , were also investigated. It was found that carbon carriers were the best, because they, in contrast to oxide carriers, are not subject to rapid degradation in corrosive hot aqueous solutions of terephthalic acid.

The results of investigating the influence of the nature of carbon carriers are known. It has been shown that active carbons prepared from vegetable, animal or mineral sources, preferably from coconut active carbon, are suitable for the production of palladium catalysts for the hydrofining of terephthalic acid. It is desirable that the surface area of such active carbons should be at least $600 \text{ m}^2/\text{g}$, and the size of granules should correspond to 3–6 mm. In US Patent No. 4728630, 1988 an additional characteristic of such active carbon is introduced, namely, the pH value of its aqueous suspension. In SU Patent No. 1660282, 1997 a possibility is disclosed of using, as a suitable carrier, an active porous carbonaceous material modified with pyrocarbon. In US Patents Nos. 4415479, 1983; 4421676, 1983; and 4791226, 1988 it is indicated that for a more effective process of the hydrofining of terephthalic acid from p-carboxybenzaldehyde it is important to prepare catalysts with a definite size of the particles of applied palladium. The size of such particles must be not greater than 35 \AA . The authors of US Patents Nos. 4394299, 1983 and 4791226, 1988 also point out a positive effect of such distribution of palladium particles in the granule of a carbon material, when they predominate on the outer surface of the granule.

In many patents it is pointed out that along with monometallic catalysts, the incorporation of Ni, Co, Cu, Fe, Mn, U, Cr, as well as Ir, Rh, Pt and Ru, into the catalyst composition may produce positive effect on the catalytic activity of palladium.

According to other group of patents [US Patents Nos. 4629715, 1986 and 4892972, 1990], the most effective action of bimetallic catalysts is attained, when the catalysts are arranged in a reactor in layers, for instance, Pd/C and Rh/C instead of one layer (Rh + Pd)/C. The authors of US Patent No. 4892972, 1990 even claim a method with the use of a layered catalyst bed, e.g., Ru/C + Rh/C + Pd/C.

Usually, catalysts comprising Group VIII metals, particularly palladium catalysts, are prepared by the adsorption of a palladium salt from solution to the carrier. In one of the processes [US Patent No. 2857337, 1967] such salt is treated with a water-soluble metal hydroxide or with a basic carbonate, this being followed by the reduction to metallic palladium with the help of such reducing agents as formaldehyde, glucose, glycerol, etc.

According to Keith et al. [US Patent No. 3138560, 1964], on addition of sodium tetrachloropalladoate or palladium chloride to many of carbon carriers, a large part of palladium immediately precipitates in the form of lustrous film of metallic palladium. Catalysts prepared by such a method usually have low activity. An opinion was voiced that palladium directly reduces to metal owing to free electrons or to the presence on the carbon surface of such functional groups as aldehydes. Palladium catalysts in the step preceding the reduction are predominantly prepared by fixing palladium in the form of an insoluble compound, so to avoid the problems of migration of palladium particles and growth of crystallites which may originate during the reduction of palladium from solution.

Though p-carboxybenzaldehyde is the most harmful impurity, which is crucial for the quality of the terephthalic acid used for the manufacture of plastics and sharply deteriorates the quality of the latter, p-toluic acid (p-TA) is also an undesirable impurity, which must be removed from the aqueous solution of terephthalic acid, obtained as a result of hydrofining. Though such removal can be achieved to a large extent owing to the greater solubility of p-toluic acid as compared to terephthalic acid, in water nevertheless substantial amounts of p-toluic acid are trapped within purified terephthalic acid crystals in the step of terephthalic acid crystallization from solution.

To avoid this disadvantage attendant to the separation of p-toluic acid, it has been proposed to decarbonylate p-carboxybenzaldehyde in aqueous solutions to benzoic acid in the presence of a palladium-on-carbon catalyst, since benzoic acid is more soluble in water than p-toluic acid [US Patent No. 3456001, 1969]. However, the foregoing decarbonylation of p-carboxybenzaldehyde to benzoic acid produces equimolar amounts of carbon monoxide, a well-known poison for the noble metals such as palladium [US Patent No. 4201872, 1980]. To minimize catalyst poisoning, in the aforementioned US Patent it is proposed to carry out the decarbonylation at relatively low process pressures so as to minimize dissolved carbon monoxide concentration in the liquid reaction medium. The process pressure also must be controlled within a closely defined pressure range. The generated carbon monoxide is purged from the reactor as a gas.

It is known [US Patent No. 4892972, 1990], that the use in the aforesaid purification of crude terephthalic acid of a catalyst system comprising a first layer of catalyst particles containing a metal of Group VIII of the Periodic Table of Elements supported on a carbon carrier and a second layer of palladium-on-carbon catalyst particles and the passage of the

aqueous solution of crude terephthalic acid through the aforesaid first layer of rhodium-on-carbon catalyst particles and then through the second layer of palladium-on-carbon catalyst particles permits the amount of p-toluic acid produced during purification of crude terephthalic acid to be minimized. Such method of using the aforesaid catalyst system does not promote the hydrogenation of p-carboxybenzaldehyde to p-toluic acid but instead promotes the decarbonylation of p-carboxybenz-aldehyde to benzoic acid, which is more soluble than p-toluic acid in water and thus is more readily separable than p-toluic acid from terephthalic acid upon crystallization of the latter. This permits a feed solution having a relatively higher p-car-boxybenzaldehyde content to be processed more economically.

The closest method of purification is described in GB Patent No. 1578725, 1980, wherein the authors propose to use catalysts comprising 2 or more metals such as Pt, Pd, Rh, Ru, Os, Ir, Fe, Ni, Co, Cr, Mn and U, in which one of the metals is Pd or Pt. In said catalysts metals are in the form of an alloy, a physical mixture, or are applied to an active carbon support (3 to 6 mm granules). Hydrofining is carried out by treating a terephthalic acid solution with hydrogen in the presence of said catalysts at elevated temperatures (280°C) and a pressure (~ 100 atm.). The rate of hydrogenation in the presence of a bimetallic catalyst (0.4% Pd-0.1% Pt)/C per gram of the catalyst is 20% higher than with the use of 0.5% Pd/C.

So, crude terephthalic acid containing p-carboxybenz-aldehyde and other impurities can be purified by hydrogenation over conventionally prepared catalysts based on Group VIII metals applied to carbon.

Brief of Summary of the Invention

The present invention solves the problem of providing selective and stable catalysts and processes, wherein crude terephthalic acid with a high initial content of p-

carboxybenz-aldehyde would be selectively hydrogenated and/or decarboxylated into benzoic acid with a low residual content of p-carboxybenz-aldehyde.

Said problem is solved in the following manner: by using in a method for the purification of terephthalic acid a catalyst composition comprising crystallites of catalytically active palladium or palladium and at least one metal of Group VIII of the Periodic Table of Elements, applied to the surface of a carbon material, wherein a mesoporous graphite-like material with the average mesopore size in the range of from 40 to 400 Å, the proportion of the mesopores in the total pore volume of at least 0.5, and the degree of graphite-similarity of at least 20% is used as the carbon material, in which metal crystallites are distributed in the volume of the carbon material granules in such a manner that the distribution peaks of these crystallites should be at a distance from the outer surface of the granule corresponding to 1-30% of its radius.

The catalyst composition comprises crystallites of palladium and rhodium or of palladium and ruthenium, or of palladium and platinum; the total content of the metals varies within the range of from 0.3 to 3.0 percent by weight, the weight ratio of palladium to other metals varies within the range of from 0.1 to 10.0

The problem is also solved by the provision of a method of preparing a catalyst composition for the purification of terephthalic acid by applying catalytically active palladium or palladium and at least one of Group VIII metals to the surface of granules of a carbon carrier, with said granules being in contact with an aqueous solution of palladium salts or palladium salts and at least one of Group VIII metals to produce a metal salt-porous carbon precursor, in which method the precursor is dried and treated with a reducing agent in an amount sufficient for reducing the superficial metal salts to metal crystallites, wherein a mesoporous graphite-like

material with the average mesopore size in the range of from 40 to 400 Å, the proportion of the mesopores in the total pore volume of at least 0.5, and the degree of graphite-similarity of at least 20% is used as the carbon material to produce a monometallic or bimetallic catalyst.

Said catalyst composition is prepared with the use of one of the following metal precursors:

H_2PdCl_4 or $Pd(NO_3)_2$;

H_2PdCl_4 or $RuOCl_3$ or $RuNO(NO_3)_3$;

$Pd(NO_3)_2$ and $RuOHCl_3$ or $RuNO(NO_3)_3$.

For preparing said catalyst composition, nitrate solutions of palladium and/or ruthenium salts are prepared with concentration of free nitric acid from 37 to 170 g/l. Bimetallic catalysts are prepared by applying metal precursors simultaneously or in succession.

We have found that such catalyst can be prepared, if mono- or bimetallic particles of Group VIII metals are applied to the surface of carbon materials having an average pore size of 40 to 200 Å and a considerable (from 20 to 60%) degree of graphite similarity; said metallic particles being distributed within the volume of the carbon carrier in such a manner that their distribution peaks are at a distance from the outer surface of said granule, equivalent to 1-30% of its radius.

As the aforesaid carbon materials carriers may be used, prepared by the heat treatment of plastics, and also synthesized in accordance with a special technology from gaseous hydro-carbons (V.A. Likhoborov et al., React. Kin. Cat. Lett., vol. 54, 2 (1995) 381-411), namely, Sibunit, KVV and various compos-ites based thereon. The physicochemical characteristics of some carbons are presented in Table 1. The tabulated data indicate that the aforesaid carbon materials in the set of such parameters as V_{meso}/V_{Σ} and K sharply differ from conventional active carbons usually employed for producing

catalysts for the hydrofining of terephthalic acid, prepared from vegetable, animal or mineral sources, preferably coconut active carbons that are used for preparing conventional terephthalic acid hydrofining catalysts.

5 We have also found that if in the pores of such carbon materials the distribution of metal particles over the volume of the carrier granule is effected in such a manner that the distribution peak(s) will be found at as distance from the outer surface of the granule corresponding to 1-30% of its
10 radius, then such catalyst has an enhanced service life on reuse. This effect is particularly manifest, when palladium and ruthenium are used as Group VIII metals. Furthermore, the presence of both palladium and ruthenium in the catalyst leads to the effect of synergism, rather than additive growth of the
15 catalyst activity, especially if the distribution peaks of the particles of these metals are in the area adjacent to the outer surface of the catalyst granules.

We have also found that with such distribution of palladium and ruthenium particles in the granule of the
20 mesoporous carbon material it is possible to replace a part of palladium by ruthenium, this leading not only to lower costs of the catalyst (since ruthenium is substantially cheaper than palladium), but also to a change in the ratio of concentrations of p-toluic and benzoic acids, which are the
25 products of p-carboxybenzaldehyde conversion, towards the latter, this promoting the attaining of a higher quality of the obtained crystalline terephthalic acid.

For preparing the aforementioned catalysts, i.e., the catalysts containing mono- or bimetallic particles of
30 palladium and ruthenium, applied to the surface of carbon carriers, it is possible to use such methods well-known in the literature as impregnating the carrier with solutions of various salts of palladium and ruthenium. However, as has been found, the best catalysts are obtained by using a method of

spray-depositing acid solution of palladium and ruthenium salts on a suitable carbon carrier with subsequent treatment of the thus applied metal precursors with hydrogen.

Examples 1-35 presented hereinbelow characterize the catalysis compositions and methods of preparing them. Examples 7, 30-34 are given for comparison, and Examples 8 and 35 are given as a prototype. Examples 36-39 describe the employed methods of purifying terephthalic acid. Analytical results concerning the character of distribution of metallic particles inside the granule of the carrier and the quality of terephthalic acid purified with the use of the proposed compositions are presented in Tables 2-6.

Example 1. A cylindrical rotated reactor is charged with 50 g of carbon carrier Sibunit 1 (the data on its physicochemical and texture properties are presented in Table 1). Here and in the Examples that follow the carrier is preliminarily purified from dust by boiling in distilled water. Then the carrier is discharged onto a sieve with 1 mm meshes and dried at 120°C to constant weight. Aqueous solutions of Na₂CO₃ (0.364 mole/l; 13 ml) and H₂PdCl₄ (0.182 mole/l; 13 ml) with the same space velocity (2.5 ml/min) in the molar ratio Na₂CO₃:H₂PdCl₄ = 2:1 are fed to a nozzle, and the resulting mixture is sprayed into the reactor. The catalyst is discharged and dried under vacuum at 75°C to constant weight. The subsequent operation of reducing is carried out in a tubular reactor it a flow of hydrogen at the temperature of 250°C for 2 hours. Then the temperature is lowered from 250°C to 40°C, at 110°C hydrogen being displaced by nitrogen. The catalyst is washed with distilled water till the absence of the reaction with AgNO₃ for chlorine ions in the washwater, and dried under vacuum at 75°C to constant weight. The procedure yields a Pd/Sib.1 catalyst with palladium content of 0.5 percent by weight. The electron probe microanalysis of the catalyst granules is carried out by

scanning the granule section along the diameter on a MAR-3
micoanalyzer with a 1-2 μm diameter probe with accelerating
voltage of 20 kV and current of 20-30 nA. As the
characteristic of the active component distribution over the
5 catalyst grain parameter Δ is used, which characterizes the
thickness of the active metal layer in μm at 1/2 of the peak
height.

The data on the distribution of palladium and ruthenium
particles in the catalysts prepared in accordance with the
10 Examples given in the present specification are listed in
Table 2.

Example 2. The catalyst is prepared as in Example 1, but
instead of an aqueous solution of H_2PdCl_4 RuOHCl_3 is used
(0.191 mole/l, 13 ml), and the concentration of the Na_2CO_3
15 solution (13 ml) corresponds to 0.382 mole/l; $\text{Na}_2\text{CO}_3:\text{RuOHCl}_2 =$
2:1. The procedure gives a Ru/Sib.1 catalyst with ruthenium
content of 0.5 percent by weight.

Example 3. The catalyst is prepared by combined
application of Ru and Pd, using aqueous solutions of RuOHCl_3
20 and H_2PdCl_4 as metal precursors, respectively. For this
purpose, a cylindrical rotated reactor is charged with 50 g of
Sibunit 1 carbon carrier. 13 ml of an aqueous solution of
 Na_2CO_3 (0.371 mole/l) and 13 ml of H_2PdCl_4 (0.109 mole/l) +
 RuOHCl_3 (0.076 mole/l) are fed to a nozzle with the same space
25 velocity (2.5 ml/min) in the molar ratio $\text{Na}_2\text{CO}_3:(\text{Ru}+\text{Pd}) = 2:1$,
and the resulting mixture is sprayed into the reactor. The
catalyst is discharged and dried under vacuum at 70°C to
constant weight. The subsequent operations of reducing,
washing and drying are similar to Example 1. The resulting
30 product is a (Ru-Pd)/Sib.1 catalyst containing 0.2 percent by
weight of ruthenium and 0.3 percent by weight of palladium.

Example 4. A cylindrical rotated reactor is charged with
50 g of Sibunit 1 carbon carrier. 26 ml of nitric aqueous

solution of $\text{Pd}(\text{NO}_3)_2$ (0.091 mole/l) with the concentration of free HNO_3 equal to 170 g/l are fed to a nozzle and the resulting mixture is sprayed with the velocity of 5 ml/min into the reactor. The sample is placed into a tubular reactor and dried in a flow of air for 1 hour, while raising the temperature to 120°C , and then kept at this temperature for another 2 hours. Then the air is replaced by nitrogen and the temperature is raised to 250°C (at this temperature decomposition of $\text{Pd}(\text{NO}_3)_2$ to palladium oxide occurs). Under these conditions the sample is kept for 3 hours and then cooled down to 150°C . Then nitrogen is replaced at this temperature by hydrogen, and the catalyst is reduced for 1 hour at 150°C , followed by raising the temperature to 250°C and keeping the sample at this temperature for 2 hours. Then the temperature is lowered from 250°C to 40°C , at 110°C hydrogen being displaced by nitrogen. The resulting product is a Pd/Sib.1 catalyst containing 0.5 percent by weight of palladium. The catalyst thus prepared is used in Examples 24, 25 in the synthesis of bimetallic catalysts.

Example 5. The catalyst is prepared as in Example 4, but instead of the aqueous nitric acid solution of $\text{Pd}(\text{NO}_3)_2$ 26 ml of an aqueous nitric acid solution of $\text{RuNO}(\text{NO}_3)_3^1$ (0.091 mole/l) with the concentration of free HNO_3 equal to 170 g/l. The resulting product is a Ru/Sib.1 catalyst containing 0.5 percent by weight of ruthenium.

Example 6. The catalyst is prepared by combined application of Ru and Pd, using aqueous nitric acid solutions of $\text{RuNO}(\text{NO}_3)_3$ and $\text{Pd}(\text{NO}_3)_2$ as metal precursors, respectively. For this purpose, a cylindrical rotated reactor is charged with 50 g of Sibunit 1 carbon carrier. 26 ml of an aqueous

¹ $\text{RuNO}(\text{NO}_3)_3$ is prepared by evaporating aqueous RuOHCl_3 to a syrupy state, dissolving the residue in concentrated HNO_3 , and subsequently evaporating the solution to the syrupy state. Then concentrated HNO_3 is added, and the evaporation is carried out again. The residue is dissolved in water to the required concentration of Ru.

nitric acid solution of $\text{RuNO}(\text{NO}_3)_3$ (0.038 mole/l) + $\text{Pd}(\text{NO}_3)_2$ (0.054 mole/l) with the concentration of free HNO_3 equal to 170 g/l are fed to a nozzle and sprayed with the velocity of 5 ml/min into the reactor. Subsequent operations of drying, calcining and reducing are similar to those used in Example 4. The resulting product is a (Ru-Pd)/Sib.1 catalyst containing 0.2 percent by weight of ruthenium and 0.3 percent by weight of palladium.

Example 7 (comparative). The catalyst is prepared as in Example 4, but instead of the Sibunit 1 carbon carrier CG-5 coconut carbon is used. The resulting product is a Pd/CG-5 catalyst containing 0.5 percent by weight of palladium.

Example 8 (prototype). The catalyst is prepared as in Example 3, but instead of the Sibunit 1 carbon carrier CG-5 coconut carbon is used. The resulting product is a (Ru-Pd)/CG-5 catalyst containing 0.2 percent by weight of ruthenium and 0.3 percent by weight of palladium.

Example 9. The catalyst is prepared as in Example 3, but 13 ml of an aqueous solution of Na_2CO_3 (0.366 mole/l) and 13 ml of H_2PdCl_4 (0.145 mole/l) + RuOCl_3 (0.038 mole/l) are fed to the nozzle; $\text{Na}_2\text{CO}_3:(\text{Ru}+\text{Pd}) = 2:1$. The resulting product is a (Ru-Pd)/Sib.1 catalyst containing 0.1 percent by weight of ruthenium and 0.4 percent by weight of palladium.

Example 10. The catalyst is prepared as in Example 3, but 13 ml of an aqueous solution of Na_2CO_3 (0.073 mole/l) + RuOCl_3 (0.115 mole/l) are fed to the nozzle; $\text{Na}_2\text{CO}_3:(\text{Ru}+\text{Pd}) = 2:1$. The resulting product is a (Ru-Pd)/Sib.1 catalyst containing 0.3 percent by weight of ruthenium and 0.2 percent by weight of palladium.

Example 11. The catalyst is prepared as in Example 6, but 26 ml of an aqueous nitric acid solution of $\text{RuNO}(\text{NO}_3)_3$ (0.019 mole/l) + $\text{Pd}(\text{NO}_3)_2$ (0.073 mole/l) with the concentration of free HNO_3 equal to 170 g/l are fed to the nozzle. The resulting

product is a (Ru-Pd)/Sib.1 catalyst containing 0.1 percent by weight of ruthenium and 0.4 percent by weight of palladium.

Example 12. The catalyst is prepared as in Example 6, but 26 ml of an aqueous nitric acid solution of $\text{RuNO}(\text{NO}_3)_3$ (0.057 mole/l) + $\text{Pd}(\text{NO}_3)_2$ (0.036 mole/l) with the concentration of free HNO_3 equal to 170 g/l are fed to the nozzle. The resulting product is a (Ru-Pd)/Sib.1 catalyst containing 0.3 percent by weight of ruthenium and 0.2 percent by weight of palladium.

Example 13. The catalyst is prepared as in Example 5, but using 26 ml of an aqueous nitric acid solution of $\text{RuNO}(\text{NO}_3)_3$ (0.038 mole/l) with the concentration of free HNO_3 equal to 53 g/l. The resulting product is Ru/Sib.1 catalyst containing 0.2 percent by weight of ruthenium. The catalyst thus prepared is used in Example 18 in the synthesis of bimetallic catalysts.

Example 14. The catalyst is prepared as in Example 13, but using 26 ml of an aqueous nitric acid solution of $\text{RuNO}(\text{NO}_3)_3$ (0.038 mole/l) with the concentration of free HNO_3 equal to 170 g/l. The resulting product is Ru/Sib.1 catalyst containing 0.2 percent by weight of ruthenium. The catalyst thus prepared is used in Example 19 in the synthesis of bimetallic catalysts.

Example 15. The catalyst is prepared as in Example 4, but using 26 ml of an aqueous nitric acid solution of $\text{Pd}(\text{NO}_3)_2$ (0.054 mole/l) with the concentration of free HNO_3 equal to 53 g/l. The resulting product is a Pd/Sib.1 catalyst containing 0.3 percent by weight of palladium. The catalyst thus prepared is used in Examples 20, 22 in the synthesis of bimetallic catalysts.

Example 16. The catalyst is prepared as in Example 15, but using 26 ml of an aqueous nitric acid solution of $\text{Pd}(\text{NO}_3)_2$ (0.054 mole/l) with the concentration of free HNO_3 equal to 170 g/l. The resulting product is a Pd/Sib.1 catalyst containing 0.3 percent by weight of palladium. The catalyst thus prepared

is used in Example 21 in the synthesis of bimetallic catalysts.

Example 17. The catalyst is prepared as in Example 1, but with feeding to the nozzle with the same space velocity (2.5 ml/min) in the molar ratio $\text{Na}_2\text{CO}_3:\text{H}_2\text{PdCl}_4 = 2:1$ aqueous solutions of Na_2CO_3 (0.218 mole/l; 13 ml) and H_2PdCl_4 (0.109 mole/l; 13 ml). The resulting product is a Pd/Sib.1 catalyst containing 0.3 percent by weight of palladium. The catalyst thus prepared is used in Example 23 in the synthesis of bimetallic catalysts.

Example 18. The catalyst is prepared as in Example 17, but using Ru/Sib.1 from Example 13 instead of Sibunit 1. The resulting product is a Pd/Ru/Sib.1 catalyst containing 0.2 percent by weight of ruthenium and 0.3 percent by weight of palladium.

Example 19. The catalyst is prepared as in Example 15, but using Ru/Sib.1 from Example 14 instead of Sibunit 1. The resulting product is a Pd/Ru/Sib.1 catalyst containing 0.2 percent by weight of ruthenium and 0.3 percent by weight of palladium.

Example 20. The catalyst is prepared as in Example 2, but with feeding to the nozzle with the same space velocity (2.5 ml/min) in the molar ratio $\text{Na}_2\text{CO}_3:\text{RuOHCl}_3 = 2:1$ aqueous solutions of Na_2CO_3 (0.152 mole/l; 13 ml) and RuOHCl_3 (0.076 mole/l; 13 ml) and using Pd/Sib.1 from Example 15 instead of Sibunit 1. The resulting product is a Ru/Pd/Sib.1 catalyst containing 0.2 percent by weight ruthenium and 0.3 percent by weight of palladium.

Example 21. The catalyst is prepared as in Example 13, but using Pd/Sib.1 from Example 16 instead of Sibunit 1. The resulting product is a Ru/Pd/Sib.1 catalyst containing 0.2 percent by weight of ruthenium and 0.3 percent by weight of palladium.

Example 22. The catalyst is prepared as in Example 14, but using Pd/Sib.1 from Example 15 instead of Sibunit 1. The resulting product is a Ru/Pd/Sib.1 catalyst containing 0.2 percent by weight of ruthenium and 0.3 percent by weight of palladium.

Example 23. The catalyst is prepared as in Example 13, but using Pd/Sib.1 from Example 17 instead of Sibunit 1. The resulting product is a Ru/Pd/Sib.1 catalyst containing 0.2 percent by weight of ruthenium and 0.3 percent by weight of palladium.

Example 24. A cylindrical rotated reactor is charged with 50 g of Pd/Sib.1 prepared as described in Example 4. An aqueous solution of H_2PtCl_6 (0.00999 mole/l; 26 ml) is fed to the nozzle and sprayed with the velocity of 5 ml/min into the reactor. The subsequent operations of reducing, washing and drying are similar to those in Example 1. The resulting product is a Pt/Pd/Sib.1 catalyst containing 0.1 percent by weight of platinum and 0.5 percent by weight of palladium.

Example 25. The catalyst is prepared as in Example 24, but using an aqueous solution of RhCl_3 (0.019 mole/l; 26 ml) instead of H_2PtCl_6 . The resulting product is a Rh/Pd/Sib.1 catalyst containing 0.1 percent by weight of rhodium and 0.5 percent by weight of palladium.

Examples 26-27. Catalysts are prepared in Example 4, but the concentration of free HNO_3 is 37 g/l (Example 26) and 147 g/l (Example 27). The resulting products are Pd/Sib.1 catalysts containing 0.5 percent by weight of palladium.

Example 28. The catalyst is prepared as in Example 1, but with feeding to the nozzle 13 ml of an aqueous solution of Na_2CO_3 (0.727 mole/l) and 13 ml of H_2PdCl_4 (0.363 mole/l); $\text{Na}_2\text{CO}_3:\text{Pd} = 2.1$. The resulting product is a Pd/Sib.1 catalyst containing 1.0 percent by weight of palladium.

Example 29. The catalyst is prepared as in Example 1, but with feeding to the nozzle 13 ml of an aqueous solution of

Na_2CO_3 (1.453 mole/l) and 13 ml of H_2PdCl_4 (0.727 mole/l); $\text{Na}_2\text{CO}_3:\text{Pd} = 2.1$. The resulting product is a Pd/Sib.1 catalyst containing 2.0 percent by weight of palladium.

5 *Example 30 (comparative)*. The catalyst is prepared as in Example 4, but using AR-B active carbon instead of Sibunit 1 carbon carrier. The resulting product is a Pd/AR-B catalyst containing 0.5 percent by weight of palladium.

10 *Example 31 (comparative)*. The catalyst is prepared as in Example 4, but using L-2702 active carbon instead of Sibunit 1 carbon carrier. The resulting product is a Pd/L-2702 catalyst containing 0.5 percent by weight of palladium.

15 *Example 32 (comparative)*. The catalyst is prepared as in Example 4, but using FB-4 active carbon instead of Sibunit 1 carbon carrier. The resulting product is a Pd/FB-4 catalyst containing 0.5 percent by weight of palladium.

Example 33 (comparative). The catalyst is prepared as in Example 1, but using KVVU-1 carbon material instead of Sibunit 1 carbon carrier. The resulting product is a Pd/KVVU-1 catalyst containing 0.5 percent by weight of palladium.

20 *Example 34 (comparative)*. The catalyst is prepared as in Example 1, but using CG-5 coconut carbon instead of Sibunit 1 carbon carrier. The resulting product is a Pd/CG-5 catalyst containing 0.5 percent by weight of palladium.

25 *Example 35 (prototype)*. The catalyst is prepared by combined application of Ru and Pd, using aqueous solutions of H_2PtCl_6 and H_2PdCl_4 as metal precursors, respectively. For this purpose, a cylindrical rotated reactor is charged with 50 g of CG-5 coconut carbon. 13 ml of an aqueous solution of Na_2CO_3 (0.330 mole/l) and 13 ml of H_2PdCl_4 (0.145 mole/l) + H_2PtCl_6 (0.020 mole/l) are fed to a nozzle with the same space velocity (2.5 ml/min) in the molar ratio $\text{Na}_2\text{CO}_3:(\text{Pt}+\text{Pd}) = 2:1$, and the resulting mixture is sprayed into the reactor. The catalyst is discharged and dried under vacuum at 70°C to constant weight. The subsequent operations of reducing,

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washing and drying are similar to Example 1. The resulting product is a (Pt-Pd)/CG-5 catalyst containing 0.1 percent by weight of platinum and 0.4 percent by weight of palladium.

Example 36. A stainless steel pot of a 457 Mini Parr
5 Reactor is charged with 150 ml of distilled H₂O and 12.9 g of impure terephthalic acid containing 8000 ppm of p-carboxybenzaldehyde and 126 ppm of p-toluic acid. The mixer rotor is modified in such a manner that it comprises a mesh basket adapted to receive catalyst granules. 0.170 g of
10 granules of the catalyst prepared as described in Example 1 is placed on the bottom of the basket. The basket is secured on the rod of the mixer. Then an autoclave cover is placed onto the pot and screwed down tightly. The reactor is connected to the system. The system is purged with nitrogen, then with
15 hydrogen, and the pressure is built up with hydrogen to 14 atm. The temperature on the control panel is set to be 250°C and the furnace heating is switched on. As the temperature in the reactor reaches the preset value, a stilling device equipped with a magnetic drive (whose rotation speed is ~ 240
20 rpm) is switched on. The time when the stirring is started is recognized as the commencement of the experiment. The experiment lasts for 3 hours. The reaction mass is then cooled, and the setup is purged with nitrogen. After that the reactor is opened, the basket with the catalyst is
25 disconnected from the rod of the mixer, and the catalyst is removed. The contents of the autoclave (a suspension of terephthalic acid in water) are transferred to a glass filter, washed with distilled water (50 ml) and dried under vacuum at 75°C for 2 hours. From the resulting terephthalic acid powder
30 samples are taken for impurity analysis.

The content of p-carboxybenzaldehyde in purified terephthalic acid is determined with the help of an OH-105 universal polarograph by voltammetric techniques in differential polariz-ation mode on a mercury-graphite

electrode in accordance with an analytical signal with a maximum at the potential of -1.07 V, proportional to the concentration of p-carboxybenzaldehyde in terephthalic acid.

The concentration of p-toluic acid in purified terephthalic acid is determined by high-pressure liquid chromatography techniques on a Milichrom liquid chromatograph. A batch of terephthalic acid is dissolved in 0.3M $\text{NH}_4\text{H}_2\text{PO}_4$ and analyzed on a 2x80 mm column with anion-exchange resin Partisil, 10 SAX (Watman) as the stationary phase.

The color level (transparence) of purified terephthalic acid is determined by measuring directly the optical density of aqueous-alkaline solutions at 340 and 400 nm. For this purpose, 1.5 g of purified terephthalic acid is dissolved in 10 ml of 2M KOH solution. The solution is preliminarily centrifugated for 15 min with the rotation speed of 3000 rpm. The optical density is measured on a spectrophotometer (in our case on a Specord M40) in 10 mm-thick quartz cells against 2M KOH solution at 340 and 400 nm.

The analytic data on the quality of terephthalic acid purified by this method on the catalysts prepared in accordance with the Examples presented hereinabove are given in Table 3.

Example 37. The method of purifying terephthalic acid is similar to that described in Example 35, the difference being in that 0.340 g of the catalyst is charged into the basket. The catalyst after the experiment (cycle) is washed directly in the basket with distilled water and used in the next cycle. The duration of testing one sample is from four to five cycles.

The analytic data on the quality of terephthalic acid purified by this method on the catalysts prepared in accordance with the Examples presented hereinabove are listed in Table 4.

Example 38. The method of purifying terephthalic acid is similar to that described in Example 36, the difference being in that the purification is carried out on the catalysts prepared as described in Examples 3 and 34 with an increased
5 initial content of p-carboxybenzaldehyde, equal to 30,000 ppm.

The analytic data on the quality of terephthalic acid purified by this method are presented in Table 5.

Example 39. 500 ml of distilled H₂O, 25 g of impure terephthalic acid containing 3552 ppm of 126 ppm of p-toluic
10 acid are charged into a 750 ml stainless steel cylinder (solvent). After that the autoclave cover is put onto the cylinder and screwed down tightly. 2.0 g of the catalyst prepared as described in Example 1 are placed on a grid of a reactor comprising a stainless steel tube with an inner
15 diameter of 10 mm, having a drain opening at the height of 110 mm from a lower grid, and fixed from the top with the second grid. The reactor is coupled to the solvent. The drain opening of the reactor via a thermostated steel capillary is tightly coupled to a crystallizer which comprises stainless steel
20 autoclave having a capacity of 750 ml. The solvent, reactor and crystallizer are disposed in a heated temperature-controlled cabinet. The system is purged with nitrogen, then with hydrogen, H₂ being bubbled through the aqueous suspension of terephthalic acid in the solvent, and the pressure is
25 brought up to 10 atm with hydrogen. On the control panel the temperature is set to be 250°C, and heating of the temperature-controlled cabinet is switched on. As soon as the temperature in the system reaches the prescribed value, hydrogen is supplied to the solvent with a constant space
30 velocity by means of a gas flow regulator. Constant pressure in the system is maintained by keeping a pressure regulator disposed at the crystallizer outlet in "pulled back" position. As the gas gradually enters the system, it displaces the terephthalic acid solution from the solvent into the reactor,

and the terephthalic acid solution is forced with a constant velocity through the catalyst bed from bottom upwards and drained through the drain opening into the crystallizer. Forcing the solution through the reactor takes 8 hours. The
5 reaction mass is cooled down, and the setup is purged with nitrogen. The contents of the crystallizer (terephthalic acid suspension in water) are transferred to a glass filter, filtered, washed with distilled water (100 ml), and dried under vacuum at 75°C for 2 hours. From the powder of
10 terephthalic acid thus obtained samples are taken for impurity analysis.

The analytic data on the quality of terephthalic acid purified by this method on the catalysts prepared in accordance with the Examples presented hereinabove are listed
15 in Table 6.

As is seen from the Examples and Tables, the proposed invention permits purifying terephthalic acid to a low residual content of p-carboxybenzaldehyde, which makes the proposed method of purifying widely applicable in the chemical
20 industry.

Table 1. Main characteristics of some granulated porous carbon materials

| Nos. | Grade | Origin (source) | Appearance | Size, mm | $A_{\text{BET}}^{1)}$, m^2/g | $V_{\text{micro}}^{2)}$, cm^3/g | $V_{\text{meso}}^{3)}$, cm^3/g | $V_{\Sigma}^{4)}$, cm^3/g | $V_{\text{meso}}/V_{\Sigma}$ | $D_{\text{mean}}^{5)}$, \AA | $K^{6)}$, % |
|------|-----------|-----------------|------------|----------|---|--|---|--|------------------------------|---------------------------------------|--------------|
| 1 | AR-B | Coal | Rod-like | 4-5 | 438 | 0.192 | 0.027 | 0.219 | 0.12 | 20 | 5 |
| 2 | CG-5 | Coconut carbon | Crushed | 3-6 | 1024 | 0.438 | 0.047 | 0.485 | 0.10 | 19 | 10 |
| 3 | L-2702 | Coal | Rod-like | 4-8 | 1024 | 0.453 | 0.046 | 0.499 | 0.03 | 19 | |
| 4 | FB-4 | Coal | Rod-like | 4-6 | 606 | 0.222 | 0.144 | 0.366 | 0.39 | 24 | |
| 5 | KVU-1 | Hydrocarbons | Granule | 3-5 | 120 | 0.010 | 0.310 | 0.32 | 0.97 | 107 | 40 |
| 6 | Sibunit 1 | Hydrocarbons | Granule | 2-3 | 440 | 0.015 | 0.665 | 0.680 | 0.98 | 62 | 60 |

1) A_{BET} (m^2/g) is the specific surface area according to BET. The surface area was calculated within the isotherm region where $P/P_0 = 0.05-0.20$; the value of the nitrogen molecule area in the filled monomolecular layer was assumed to be equal to $\omega = 0.162 \text{ nm}^2$;

2) V_{micro} (cm^3/g) is the volume of micropores. It was calculated, using comparative method within isotherm regions corresponding to the region between the filling of micropores and the onset of capillary condensation; the value V_{micro} corresponds to the total volume of ultramicro- and supermicropores, that is, to the volume of micropores whose size is smaller than 20 \AA ;

3) V_{meso} (cm^3/g) = $V_{\Sigma} - V_{\text{micro}}$;

4) V_{Σ} (cm^3/g) is the volume of pores whose size is smaller than 5000 \AA . It is calculated from the adsorption of nitrogen at $P/P_0 = 0.98$;

5) D_{mean} (\AA) is the mean size of pores, calculated as $D_{\text{mean}} = 4 \cdot 10^4 \cdot V_{\Sigma} / A_{\text{BET}}$;

6) K (%) is the degree of crystallinity, calculated from the integral peak intensity (002); diffractograms were recorded on a HZG-4C diffractometer ($\text{CuK}\alpha$, graphite monochromator).

Table 2. Properties of the catalysts

| Example No. | Catalyst composition, percent by weight | Distribution of metal over the granule, μm | | | | |
|-------------|---|---|------------------------------|-------------|---------------------------|------------|
| | | $\Delta^1)$ Ru | $\Delta_{\text{mean}}^2)$ Ru | Δ Pd | Δ_{mean} Pd | |
| 1 | 0.5% Pd/Sib.1 | | | 27-75 | | 38 |
| 2 | 0.5% Ru/Sib.1 | 18-45 | 32 | | | |
| 3 | (0.2% Ru-0.3% Pd)/Sib.1 | 30-91 | 44 | 19-82 | | 38 |
| 4 | 0.5% Pd/Sib.1 | | | 58-410 | | 302 |
| 5 | 0.5% Ru/Sib.1 | 220-384 | 293 | | | |
| 6 | (0.2% Ru-0.3% Pd)/Sib.1 | 90-339 | 240 | 90-298 | | 249 |
| 7 | 0.5% Pd/CG-5 | | | 18-75 | | 41 |
| 8 | (0.2% Ru-0.3% Pd)/CG-5 | 12-48 | 26 | 9-42 | | 22 |
| 10 | (0.3% Ru-0.2% Pd)/Sib.1 | | | 22-79 | | 44 |
| 14 | 0.2% Ru/Sib.1 | Fuzzy | ≥ 475 | | | |
| 15 | 0.3% Pd/Sib.1 | | | 261-597 | | 371 |
| 16 | 0.3% Pd/Sib.1 | | | 477-1530 | | 988 |
| 17 | 0.3% Pd/Sib.1 | | | 17-123 | | 46 |
| 18 | 0.3% Pd/0.2% Ru/Sib.1 | 34-716 | 285 | Fuzzy | | ≥ 580 |
| 19 | 0.3% Pd/0.2% Ru/Sib.1 | Fuzzy | ≥ 766 | 56-183 | | 134 |
| 20 | 0.2% Ru/0.3% Pd/Sib.1 | 28-206 | 92 | 14-597 | | 211 |
| 21 | 0.2% Ru/0.3% Pd/Sib.1 | 178-505 | 286 | 322-1533 | | 739 |
| 22 | 0.2% Ru/0.3% Pd/Sib.1 | 64-673 | 396 | 56-1150 | | 200 |
| 23 | 0.2% Ru/0.3% Pd/Sib.1 | 159-430 | 302 | 17-239 | | 90 |
| 26 | 0.5% Pd/Sib.1 | | | 51-232 | | 121 |
| 30 | 0.5% Pd/AR-B | | | 45-250 | | 128 |
| 31 | 0.5% Pd/L-2702 | | | 58-287 | | 150 |
| 32 | 0.5% Pd/FB-4 | | | 7-29 | | 17 |
| 34 | 0.5% Pd/CG-5 | | | 6-40 | | 18 |

¹⁾ Parameter Δ characterizes the thickness of active layer in μm at 1/2 height of the peak of metal distribution in the surface layer of the granule;

²⁾ Δ_{mean} is the arithmetic mean of the parameter Δ .

Table 3. Characteristics of TPA purified by the method according to Example 36

| Example No. | Catalyst composition, percent by weight | Characteristics of purified TPA | | | |
|-------------|---|---------------------------------------|--------|----------------------------|------|
| | | Transmission of alkaline solutions, % | | Content of impurities, ppm | |
| | | 340 nm | 400 nm | p-CBA | p-TA |
| 1 | 0.5% Pd/Sib.1 | 95.51 | 98.83 | 9 | 3620 |
| 2 | 0.5% Ru/Sib.1 | 84.51 | 96.27 | 25 | 520 |
| 3 | (0.2% Ru-0.3% Pd)/Sib.1 | 93.21 | 98.42 | 12 | 2620 |
| 4 | 0.5% Pd/Sib.1 | 84.57 | 96.86 | 455 | 729 |
| 5 | 0.5% Ru/Sib.1 | 75.78 | 97.43 | 851 | 138 |
| 6 | (0.2% Ru-0.3% Pd)/Sib.1 | 89.31 | 98.47 | 345 | 524 |
| 7 | 0.5% Pd/CG-5 | 66.14 | 81.65 | 16 | 760 |
| 8 | (0.2% Ru-0.3% Pd)/CG-5 | 89.90 | 95.50 | 10 | 3696 |
| 9 | (0.1% Ru-0.4% Pd)/Sib.1 | 95.79 | 99.15 | 9 | 2830 |
| 10 | (0.3% Ru-0.2% Pd)/Sib.1 | 94.18 | 98.56 | 10 | 1640 |
| 11 | (0.1% Ru-0.4% Pd)/Sib.1 | 91.98 | 100.00 | 340 | 602 |
| 12 | (0.3% Ru-0.2% Pd)/Sib.1 | 90.82 | 100.00 | 336 | 394 |
| 13 | 0.2% Ru/Sib.1 | 69.76 | 98.16 | 1265 | 79 |
| 15 | 0.3% Pd/Sib.1 | 77.08 | 95.96 | 842 | 138 |
| 16 | 0.3% Pd/Sib.1 | 78.22 | 96.99 | 772 | 151 |
| 18 | 0.3% Pd/0.2% Ru/Sib.1 | 97.03 | 99.70 | 1402 | 197 |
| 19 | 0.3% Pd/0.2% Ru/Sib.1 | 93.08 | 100.00 | 131 | 914 |
| 20 | 0.2% Ru/0.3% Pd/Sib.1 | 86.52 | 98.67 | 446 | 743 |
| 21 | 0.2% Ru/0.3% Pd/Sib.1 | 77.66 | 97.51 | 973 | 284 |
| 23 | 0.2% Ru/0.3% Pd/Sib.1 | 77.80 | 97.51 | 1303 | 201 |
| 24 | 0.1% Pt/0.5% Pd/Sib.1 | 75.54 | 97.56 | 200 | 689 |
| 25 | 0.1% Rh/0.5% Pd/Sib.1 | 52.57 | 96.30 | 494 | 176 |
| 26 | 0.5% Pd/Sib.1 | 92.88 | 97.17 | 56 | 2251 |
| 27 | 0.5% Pd/Sib.1 | 95.00 | 98.90 | 83 | 3662 |
| 28 | 1% Pd/Sib.1 | 89.50 | 94.23 | 6 | 6048 |
| 29 | 2% Pd/Sib.1 | 100.00 | 100.00 | 15 | 5443 |
| 30 | 0.5% Pd/AR-B | 72.65 | 94.28 | 432 | 235 |
| 31 | 0.5% Pd/L-2702 | 56.28 | 99.00 | 676 | 184 |
| 32 | 0.5% Pd/FB-4 | 59.84 | 92.57 | 412 | 230 |
| 33 | 0.5% Pd/KVU-1 | 94.79 | 94.44 | 6 | 1020 |
| 34 | 0.5% Pd/CG-5 | 98.6 | 100.00 | 6 | 559 |
| 35 | (0.1% Pt-0.4% Pd)/CG-5 | 87.57 | 98.41 | 18 | 1200 |

Table 4. Characteristics of TPA purified by the method according to Example 37

| Ex. No. | Catalyst composition, Percent by weight | Cycle No. | Characteristics of purified TPA | | | |
|---------|---|-----------|---------------------------------------|--------|----------------------------|------|
| | | | Transmission of alkaline solutions, % | | Content of impurities, ppm | |
| | | | 340 nm | 400 nm | p-CBA | p-TA |
| 1 | 0.5% Pd/Sib.1 | 1 | 96.52 | 98.85 | 6 | 7249 |
| | | 2 | 97.18 | 99.52 | 5 | 6955 |
| | | 3 | 94.25 | 98.35 | 5 | 4534 |
| | | 4 | 89.90 | 95.92 | 6 | 2688 |
| | | 5 | 88.55 | 95.63 | 4 | 1058 |
| 2 | 0.5% Ru/Sib.1 | 1 | 89.86 | 97.79 | 24 | 1067 |
| | | 2 | 88.39 | 98.60 | 23 | 546 |
| | | 3 | 84.81 | 100.00 | 25 | 269 |
| | | 4 | 80.46 | 96.16 | 23 | 297 |
| | | 5 | 82.44 | 97.12 | 25 | 199 |
| 3 | (0.2% Ru-0.3% Pd)/Sib.1 | 1 | 95.80 | 99.17 | 11 | 1873 |
| | | 2 | 96.64 | 100.00 | 10 | 1528 |
| | | 3 | 97.50 | 100.00 | 9 | 1218 |
| | | 4 | 89.19 | 96.25 | 14 | 974 |
| | | 5 | 84.46 | 94.30 | 15 | 907 |
| 6 | (0.2% Ru-0.3% Pd)/Sib-1 | 1 | 93.80 | 99.08 | 6 | 1890 |
| | | 2 | 92.06 | 97.08 | 8 | 1033 |
| | | 3 | 90.51 | 97.42 | 53 | 949 |
| | | 4 | 88.76 | 97.47 | 85 | 1117 |
| | | 5 | 82.00 | 97.85 | 206 | 1151 |
| 7 | 0.5% Pd/CG-5 | 1 | 98.11 | 100.00 | 5 | 4402 |
| | | 2 | 97.74 | 100.00 | 7 | 1381 |
| | | 3 | 94.78 | 99.08 | 12 | 748 |
| | | 4 | 91.95 | 99.22 | 52 | 882 |
| 8 | (0.2% Ru-0.3% Pd)/CG-5 | 1 | 99.27 | 100.00 | 9 | 5275 |
| | | 2 | 99.30 | 100.00 | 40 | 1613 |
| | | 3 | 96.53 | 100.00 | 34 | 3142 |
| | | 4 | 91.38 | 98.26 | 60 | 511 |
| | | 5 | 90.91 | 99.46 | 202 | 442 |

Table 4 (continued)

| Ex. No. | Catalyst composition, Percent by weight | Cycle No. | Characteristics of purified TPA | | | |
|---------|---|-----------|---------------------------------------|--------|----------------------------|------|
| | | | Transmission of alkaline solutions, % | | Content of impurities, ppm | |
| | | | 340 nm | 400 nm | p-CBA | p-TA |
| 19 | 0.3% Pd/0.2% Ru/Sib.1 | 1 | 93.84 | 99.18 | 12 | 7200 |
| | | 2 | 90.67 | 97.65 | 88 | 6200 |
| | | 3 | 94.78 | 100.00 | 279 | 756 |
| | | 4 | 83.80 | 96.18 | 366 | 873 |
| | | 5 | 79.52 | 95.06 | 297 | 672 |
| 20 | 0.2% Ru/0.3% Pd/Sib.1 | 1 | 97.13 | 100.00 | 8 | 1267 |
| | | 2 | 90.87 | 100.00 | 219 | 571 |
| | | 3 | 82.48 | 100.00 | 865 | 549 |
| | | 4 | 76.62 | 100.00 | 1213 | 477 |
| | | 5 | 68.24 | 96.39 | 1312 | 319 |
| 23 | 0.2% Ru/0.3% Pd/Sib.1 | 1 | 96.80 | 100.00 | 255 | 899 |
| | | 2 | 83.89 | 97.13 | 405 | 168 |
| | | 3 | 75.50 | 94.09 | 778 | 124 |
| | | 4 | 70.48 | 93.70 | 814 | 155 |
| | | 5 | 67.61 | 94.70 | 1003 | 286 |
| 26 | 0.5% Pd/Sib.1 | 1 | 97.87 | 100.00 | 10 | 2612 |
| | | 2 | 98.71 | 100.00 | 10 | 2352 |
| | | 3 | 95.33 | 100.00 | 6 | 361 |
| | | 4 | 92.26 | 99.44 | 72 | 470 |
| | | 5 | 86.55 | 97.88 | 198 | 655 |
| 34 | 0.5% Pd/CG-5 | 1 | 94.85 | 96.84 | 8 | |
| | | 2 | 95.41 | 100.00 | 11 | |
| | | 3 | 93.72 | 98.87 | 71 | |
| | | 4 | 91.28 | 97.72 | 360 | |
| | | 5 | 89.16 | 97.24 | 739 | |

Table 5. Characteristics of TPA purified by the method according to Example 38 (with the initial p-CBA content of 30,000 ppm)

| Ex. No. | Catalyst composition, Percent by weight | Cycle No. | Characteristics of purified TPA | | |
|---------|---|-----------|--|--------|-----------------------|
| | | | Transmission of alkali-line solutions, % | | Content of p-CBA, ppm |
| | | | 340 nm | 400 nm | |
| 3 | (0,2% Ru-0.3% Pd)/Sib.1 | 1 | 92.22 | 97.00 | 10 |
| | | 2 | 94.34 | 98.33 | 20 |
| | | 3 | 93.93 | 97.46 | 31 |
| | | 4 | 79.58 | 93.73 | 41 |
| | | 5 | 77.89 | 93.46 | 156 |
| 34 | 0.5% Pd/CG-5 | 1 | 97.95 | 98.54 | 9 |
| | | 2 | 91.15 | 97.67 | 37 |
| | | 3 | 88.29 | 97.68 | 434 |
| | | 4 | 72.85 | 97.52 | 1607 |
| | | 5 | 41.71 | 92.83 | 3447 |

Table 6. Characteristics of TPA purified by the method according to Example 39

| Example No. | Catalyst composition, percent by weight | Duration of experiment (t), hr | Weight of catal. (P_{wt}), g | $Lw^{1)}$ | Characteristics of purified TPA | | | |
|-------------|---|--------------------------------|----------------------------------|-----------|---------------------------------------|--------|----------------------------|------|
| | | | | | Transmission of alkaline solutions, % | | Content of impurities, ppm | |
| | | | | | 340 nm | 400 nm | p-CBA | p-TA |
| 1 | 0.5% Pd/Sib.1 | 8 | 2.00 | 29.5 | 90.7 | 97.2 | 15 | 460 |
| 3 | 0.2% Ru-0.3% Pd/Sib.1 | 10 | 2.00 | 4.2 | 92.17 | 99.21 | 32 | 1930 |
| 3 | 0.2% Ru-0.3% Pd/Sib.1 | 10 | 2.00 | 18.8 | 83.01 | 91.88 | 80 | 116 |
| 4 | 0.5% Pd/Sib.1 | 10 | 2.00 | 1.2 | | | 55 | 1242 |
| 4 | 0.5% Pd/Sib.1 | 10 | 2.00 | 20.3 | 86.6 | 99.3 | 189 | 10 |
| 7 | 0.5% Pd/CG-5 | 10 | 2.00 | 22.4 | 88.75 | 97.19 | 164 | 39 |
| 8 | 0.2% Ru-0.3% Pd/CG-5 | 10 | 2.00 | 17.3 | 92.13 | 99.27 | 100 | 152 |
| 33 | 0.5% Pd/KBU-1 | 10 | 2.00 | 20.1 | 87.81 | 98.46 | 80 | 162 |
| 34 | 0.5% Pd/CG-5 | 10 | 2.00 | 20.2 | 89.7 | 95.3 | 15 | 162 |

¹⁾ Bulk load on the catalyst $Lw = W_{TPA}/(P_{wt} \cdot t)$, where W_{TPA} is the volume of TPA solution passed through catalyst layer during the time t .

CLAIMS

1. A catalyst composition comprising crystallites of catalytically active palladium or palladium and at least one metal of Group VIII of the Periodic Table of Elements, applied to the surface of a carbon material, wherein a mesoporous graphite-like material with the average mesopore size in the range of from 40 to 400 Å, the proportion of the mesopores in the total pore volume of at least 0.5, and the degree of graphite-similarity of at least 20% is used as the carbon material, in which metal crystallites are distributed in the volume of the carbon material granules in such a manner that the distribution peaks of these crystallites should be at a distance from the outer surface of the granule corresponding to 1-30% of its radius.

2. The catalyst composition of claim 1, characterized in that it comprises crystallites of rhodium and palladium.

3. The catalyst composition of claim 1, characterized in that it comprises crystallites of palladium and ruthenium.

4. The catalyst composition of claim 1, characterized in that it comprises crystallites of palladium and platinum.

5. The catalyst composition of claim 1, characterized in that the total content of metals therein varies within the range of from 0.1 to 3.0 percent by weight.

6. The catalyst composition of claim 1, characterized in that the weight ratio of palladium to other metals varies within the range of from 0.1 to 10.0.

7. A method of preparing a catalyst composition for the purification of terephthalic acid by applying catalytically active palladium or palladium and at least one of Group VIII metals to the surface of granules of a carbon carrier, said granules being contacted with an aqueous solution of palladium salts or palladium salts and salts of at least one of Group VIII metals to produce a "metal salt - porous carbon" precursor, wherein the precursor is dried and treated with a reducing agent in an amount sufficient for reducing the surface metal salts to the

metal crystallites, characterized in that a mesoporous graphite-like material with the average mesopore size in the range of from 40 to 400 Å, the proportion of the mesopores in the total pore volume of at least 0.5, and the degree of graphite-similarity of at least 20% is used as the carbon material to produce a metallic or bimetallic catalyst.

8. The method of claim 7, characterized in that said catalyst composition is prepared, using one of the following metal precursors:

H_2PdCl_4 or $Pd(NO_3)_2$;
 H_2PdCl_4 and $RuOHCl_3$ or $RuNO(NO_3)_3$;
 $Pd(NO_3)_2$ and $RuOHCl_3$ or $RuNO(NO_3)_3$.

9. The method of claim 7, characterized in that said catalyst composition is prepared, using nitric acid solutions of palladium and/or ruthenium salts with the concentration of free nitric acid ranging from 37 to 170 g/l.

10. The method of claim 7, characterized in that bimetallic catalysts are prepared by combined application of metal precursors.

11. The method of claim 7, characterized in that bimetallic catalysts are prepared by successive application of metal precursors.

12. A method of purifying terephthalic acid from p-carboxybenzaldehyde in the presence of hydrogen with the use of a catalyst composition which comprises crystallites of catalytically active palladium or of palladium and at least one metal of Group VIII of the Periodic Table of Elements, applied to the surface of carbon material, characterized in that in the catalyst composition a mesoporous graphite-like material with the average mesopore size in the range of from 40 to 400 Å, the proportion of the mesopores in the total pore volume of at least 0.5, and the degree of graphite-similarity of at least 20% is used as the carbon material, wherein the metal crystallites are distributed within the volume of granules of the carbon material in such a manner that peaks of the distribution of active components

should be should be at a distance from the outer surface of the granule corresponding to 1-30% of its radius.

13. The method of claim 12, characterized in that the catalyst composition comprises crystallites of palladium and rhodium.

14. The method of claim 12, characterized in that the catalyst composition comprises crystallites of palladium and ruthenium.

15. The method of claim 12, characterized in that the catalyst composition comprises crystallites of palladium and platinum.

16. The method of claim 12, characterized in that the total content of metals in the catalyst composition varies within the range of from 0.1 to 3.0 percent by weight.

17. The method of claim 12, characterized in that the weight ratio of palladium to other metals in the catalyst composition varies within the range of 0.1 to 10.0.

18. The method of claim 12, characterized in that the concentration of p-carboxybenzaldehyde in terephthalic acid to be purified varies from 1000 to 30000 ppm.

Catalyst Composition, Method for Preparing thereof,
and Method for Purifying Terephthalic Acid

ABSTRACT

5

The present invention relates to catalyst compositions for purifying terephthalic acid, based on Group VIII metals, to methods for preparing thereof, and to a method of purifying terephthalic acid suitable for the subsequent synthesis of polyester polymers and copolymers used in the manufacture of textile fibers.

The present invention solves the problem of providing selective and stable catalysts and processes wherein crude terephthalic acid with a high initial content of p-carboxybenzaldehyde should be selectively hydrogenated into p-toluic acid or/and decarbonylated into benzoic acid with a low residual content of p-carboxybenzaldehyde.

Said problem is solved by using in a method for the purification of terephthalic acid a catalyst composition comprising crystallites of catalytically active palladium or of palladium and at least one metal of Group VIII of the Periodic Table of Elements, applied to the surface of a carbon material, wherein a mesoporous graphite-like material with the average mesopore size in the range of from 40 to 400 Å, the proportion of the mesopores in the total pore volume of at least 0.5, and the degree of graphite-similarity of at least 20% is used as the carbon material, in which metal crystallites are distributed in the volume of the carbon material granules in such a manner that the distribution peaks of these crystallites should be at a distance from the outer surface of the granule corresponding to 1-30% of its radius.

The catalyst composition comprises crystallites of palladium and rhodium or of palladium and ruthenium, or of palladium and platinum, the total content of the metals varying within 0.1 to 3.0 percent by weight and the weight ratio of palladium to other metals varying within 0.1 to 10.0.

Practitioner's Docket No. U 013681-9

PATENT

COMBINED DECLARATION AND POWER OF ATTORNEY

(ORIGINAL, DESIGN, NATIONAL STAGE OF PCT, SUPPLEMENTAL, DIVISIONAL,
CONTINUATION, OR C-I-P)

As a below named inventor, I hereby declare that:

TYPE OF DECLARATION

This declaration is of the following type:

(check one applicable item below)

- ☐ original.
☐ design.

NOTE: *With the exception of a supplemental oath or declaration submitted in a reissue, a supplemental oath or declaration is not treated as an amendment under 37 CFR 1.312 (Amendments after allowance). M.P.E.P. Section 714.16, 7th Ed.*

- ☐ supplemental.

NOTE: *If the declaration is for an International Application being filed as a divisional, continuation or continuation-in-part application, do not check next item; check appropriate one of last three items.*

- ☒ national stage of PCT.

NOTE: *If one of the following 3 items apply, then complete and also attach **ADDED PAGES FOR DIVISIONAL, CONTINUATION OR C-I-P.***

NOTE: *See 37 C.F.R. Section 1.63(d) (continued prosecution application) for use of a prior nonprovisional application declaration in the continuation or divisional application being filed on behalf of the same or fewer of the inventors named in the prior application.*

- ☐ divisional.
☐ continuation.

NOTE: *Where an application discloses and claims subject matter not disclosed in the prior application, or a continuation or divisional application names an inventor not named in the prior application, a continuation-in-part application must be filed under 37 C.F.R. Section 1.53(b) (application filing requirements-nonprovisional application).*

- ☐ continuation-in-part (C-I-P).

INVENTORSHIP IDENTIFICATION

WARNING: *If the inventors are each not the inventors of all the claims, an explanation of the facts, including the ownership of all the claims at the time the last claimed invention was made, should be submitted.*

My residence, post office address and citizenship are as stated below, next to my name. I believe that I am the original, first and sole inventor (*if only one name is listed below*) or an original, first and joint inventor (*if plural names are listed below*) of the subject matter that is claimed, and for which a patent is sought on the invention entitled:

TITLE OF INVENTION

Catalytic Composition, Method for Manufacturing thereof
and Method for the Purification of Terephthalic Acid

SPECIFICATION IDENTIFICATION

The specification of which:

(complete (a), (b), or (c))

(a) ☐ is attached hereto.

NOTE: "The following combinations of information supplied in an oath or declaration filed on the application filing date with a specification are acceptable as minimums for identifying a specification and compliance with any one of the items below will be accepted as complying with the identification requirement of 37 C.F.R. Section 1.63:

"(1) name of inventor(s), and reference to an attached specification which is both attached to the oath or declaration at the time of execution and submitted with the oath or declaration on filing;

"(2) name of inventor(s), and attorney docket number which was on the specification as filed; or

"(3) name of inventor(s), and title which was on the specification as filed."

Notice of July 13, 1995 (1177 O.G. 60).

(b) ☐ was filed on _____, ☐ as Application No. _____
☐ and was amended on _____ (if applicable).

NOTE: Amendments filed after the original papers are deposited with the PTO that contain new matter are not accorded a filing date by being referred to in the declaration. Accordingly, the amendments involved are those filed with the application papers or, in the case of a supplemental declaration, are those amendments claiming matter not encompassed in the original statement of invention or claims. See 37 C.F.R. Section 1.67.

NOTE: "The following combinations of information supplied in an oath or declaration filed after the filing date are acceptable as minimums for identifying a specification and compliance with any one of the items below will be accepted as complying with the identification requirement of 37 C.F.R. Section 1.63:

(A) application number (consisting of the series code and the serial number, e.g., 08/123,456);

(B) serial number and filing date;

(C) attorney docket number which was on the specification as filed;

(D) title which was on the specification as filed and reference to an attached specification which is both attached to the oath or declaration at the time of execution and submitted with the oath or declaration;

or

(E) title which was on the specification as filed and accompanied by a cover letter accurately identifying the application for which it was intended by either the application number (consisting of the series code and the serial number, e.g., 08/123,456), or serial number and filing date. Absent any statement(s) to the contrary, it will be presumed that the application filed in the PTO is the application which the inventor(s) executed by signing the oath or declaration.

M.P.E.P. Section 601.01(a), 7th ed.

- (c) ☒ was described and claimed in PCT International Application No. RU99/00477 filed on Dec. 9, 1999 and as amended under PCT Article 19 on _____ (if any).

SUPPLEMENTAL DECLARATION (37 C.F.R. Section 1.67(b))

(complete the following where a supplemental declaration is being submitted)

☐ I hereby declare that the subject matter of the

☐ attached amendment

☐ amendment filed on _____.

was part of my/our invention and was invented before the filing date of the original application, above identified, for such invention.

ACKNOWLEDGMENT OF REVIEW OF PAPERS AND DUTY OF CANDOR

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information, which is material to patentability as defined in 37, Code of Federal Regulations, Section 1.56,

(also check the following items, if desired)

☐ and which is material to the examination of this application, namely, information where there is a substantial likelihood that a reasonable Examiner would consider it important in deciding whether to allow the application to issue as a patent, and

☐ in compliance with this duty, there is attached an information disclosure statement, in accordance with 37 C.F.R. Section 1.98.

PRIORITY CLAIM (35 U.S.C. Section 119(a)-(d))

NOTE: "The claim to priority need be in no special form and may be made by the attorney or agent if the foreign application is referred to in the oath or declaration as required by Section 1 63. The claim for priority and the certified copy of the foreign application specified in 35 U.S.C. Section 119(b) must be filed in the case of an interference (Section 1.630), when necessary to overcome the date of a reference relied upon by the examiner, when specifically required by the examiner, and in all other situations, before the patent is granted. If the claim for priority or the certified copy of the foreign application is filed after the date the issue fee is paid, it must be accompanied by a petition requesting entry and by the fee set forth in Section 1.17(i). If the certified copy is not in the English language, a translation need not be filed except in the case of interference; or when necessary to overcome the date of a reference relied upon by the examiner; or when specifically required by the examiner, in which event an English language translation must be filed together with a statement that the translation of the certified copy is accurate." 37 C.F.R. Section 1.55(a).

I hereby claim foreign priority benefits under Title 35, United States Code, Section 119(a)-(d) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

(complete (d) or (e))

- (d) ☐ no such applications have been filed. .
(e) ☒ such applications have been filed as follows.

NOTE: Where item (c) is entered above and the International Application which designated the U.S. itself claimed priority check item (e), enter the details below and make the priority claim.

**PRIOR FOREIGN/PCT APPLICATION(S) FILED WITHIN 12 MONTHS
(6 MONTHS FOR DESIGN) PRIOR TO THIS APPLICATION
AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. SECTION 119(a)-(d)**

| COUNTRY (OR INDICATE IF PCT) | APPLICATION NUMBER | DATE OF FILING DAY, MONTH, YEAR | PRIORITY CLAIMED UNDER 35 USC 119 |
|------------------------------------|--------------------|------------------------------------|---|
| RU | 99116348 | 29.07.1999 | <input checked="" type="checkbox"/> YES <input type="checkbox"/> NO |
| | | | <input type="checkbox"/> YES <input type="checkbox"/> NO |
| | | | <input type="checkbox"/> YES <input type="checkbox"/> NO |
| | | | <input type="checkbox"/> YES <input type="checkbox"/> NO |
| | | | <input type="checkbox"/> YES <input type="checkbox"/> NO |

CLAIM FOR BENEFIT OF PRIOR U.S. PROVISIONAL APPLICATION(S)
(35 U.S.C. Section 119(e))

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below:

PROVISIONAL APPLICATION NUMBER

_____/_____
_____/_____
_____/_____

FILING DATE

CLAIM FOR BENEFIT OF EARLIER U.S./PCT APPLICATION(S)
UNDER 35 U.S.C. SECTION 120

[] The claim for the benefit of any such applications are set forth in the attached ADDED PAGES TO COMBINED DECLARATION AND POWER OF ATTORNEY FOR DIVISIONAL, CONTINUATION OR CONTINUATION-IN-PART (C-I-P) APPLICATION.

ALL FOREIGN APPLICATION(S), IF ANY, FILED MORE THAN 12 MONTHS
(6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION

NOTE: If the application filed more than 12 months from the filing date of this application is a PCT filing forming the basis for this application entering the United States as (1) the national stage, or (2) a continuation, divisional, or continuation-in-part, then also complete ADDED PAGES TO COMBINED DECLARATION AND POWER OF ATTORNEY FOR DIVISIONAL, CONTINUATION OR C-I-P APPLICATION for benefit of the prior U.S. or PCT application(s) under 35 U.S.C. Section 120.

POWER OF ATTORNEY

I hereby appoint the following practitioner(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

(list name and registration number)

JOSEPH H. HANDELMAN, 26179

JOHN RICHARDS, 31053

RICHARD J. STREIT, 25765

PETER D. GALLOWAY, 27885

IAN C. BAILLIE, 24090

THOMAS F. PETERSON, 24790

RICHARD P. BERG, 28145

JULIAN H. COHEN, 20302

WILLIAM R. EVANS, 25858

JANET I. CORD, 33778

CLIFFORD J. MASS, 30086

CYNTHIA R. MILLER, 34678

(Check the following item, if applicable)

[] I hereby appoint the practitioner(s) associated with the Customer Number provided below to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

[] Attached, as part of this declaration and power of attorney, is the authorization of the above-named practitioner(s) to accept and follow instructions from my representative(s).

NOTE: "Special care should be taken in continuation or divisional applications to ensure that any change of correspondence address in a prior application is reflected in the continuation or divisional application. For example, where a copy of the oath or declaration from the prior application is submitted for a continuation or divisional application filed under 37 CFR 1.53(b) and the copy of the oath or declaration from the prior application designates an old correspondence address, the Office may not recognize, in the continuation or divisional application, the change of correspondence address made during the prosecution of the prior application. Applicant is required to identify the change of correspondence address in the continuation or divisional application to ensure that communications from the Office are mailed to the current correspondence address. 37 CFR 1.63(d)(4)." Section 601.03, M.P.E.P., 7th Ed.

SEND CORRESPONDENCE TO

DIRECT TELEPHONE CALLS TO:
(Name and telephone number)

Ladas & Parry
26 West 61st Street
New York, N.Y. 10023

(complete the following if applicable)

Since this filing is a [] continuation [] divisional there is attached hereto a Change of Correspondence Address so that there will be no question as to where the PTO should direct all correspondence.

DECLARATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

SIGNATURE(S)

NOTE: Carefully indicate the family (or last) name, as it should appear on the filing receipt and all other document.

NOTE: Each inventor must be identified by full name, including the family name, and at least one given name without abbreviation together with any other given name or initial, and by his/her residence, post office address and country of citizenship. 37 C.F.R. Section 1.63(a)(3).

NOTE: Inventors may execute separate declarations/oaths provided each declaration/oath sets forth all the inventors. Section 1.63(a)(3) requires that a declaration/oath, inter alia, identify each inventor and prohibits the execution of separate declarations/oaths which each sets forth only the name of the executing inventor. 62 Fed. Reg. 53,131, 53,142, October 10, 1997,

Full name of sole or first inventor

1-0
Anatoly Vladimirovich Romanenko
(Given Name) (Middle Initial or Name) Family (Or Last Name)

Inventor's signature Анатолий Владимирович Романенко

Date April 19, 2002 Country of Citizenship Russia

Residence Russia, Novosibirsk RUX

Post Office Address Russia, Novosibirsk, ulitsa Shljuzovaya 22,
kv. 52

Full name of second joint inventor, if any

2-0
Vladimir Alexandrovich Likholobov
(Given Name) (Middle Initial or Name) Family (Or Last Name)

Inventor's signature Владимир Александрович Лихолобов

Date April 19, 2002 Country of Citizenship Russia

Residence Russia, Novosibirsk RUX

Post Office Address Russia, Novosibirsk, ulitsa Detsky proezd, 9,
kv. 8

Full name of third joint inventor, if any

3-0
Maria Nikolaevna Timofeevna
(Given Name) (Middle Initial or Name) Family (Or Last Name)

Inventor's signature Мария Николаевна Тимофеева

Date April 19, 2002 Country of Citizenship Russia

Residence Russia, Novosibirsk RUX

Post Office Address Russia, Novosibirsk, ulitsa Morskoi prospekt,
48; kv. 50

(check proper box(es) for any of the following added page(s)
that form a part of this declaration)

☒ **Signature** for fourth and subsequent joint inventors. *Number of pages added* 1

* * *

☐ **Signature** by administrator(trix), executor(trix) or legal representative for deceased or incapacitated inventor. *Number of pages added* _____

* * *

☐ **Signature** for inventor who refuses to sign or cannot be reached by person authorized under 37 C.F.R. Section 1.47. *Number of pages added* _____

* * *

☐ Added page for **signature** by one joint inventor on behalf of deceased inventor(s) where legal representative cannot be appointed in time. (37 C.F.R. Section 1.47)

* * *

☐ Added pages to combined declaration and power of attorney for divisional, continuation, or continuation-in-part (C-I-P) application.

☐ Number of pages added _____

* * *

☐ Authorization of practitioner(s) to accept and follow instructions from representative.

(If no further pages form a part of this Declaration,
then end this Declaration with this page and check the following item)

☐ This declaration ends with this page.

in care, the family (or last) name,

NOTE: *Inventors may execute separate declarations/oaths provided each declaration/oath sets forth all the inventors. Section 1.63(a)(3) requires that a declaration/oath, inter alia, identify each inventor and prohibits the execution of separate declarations/oaths which each sets forth only the name of the executing inventor. 62 Fed. Reg. 53,131, 53,142, October 10, 1997,*

Sung Hwa JHUNG
(Given Name) (Middle Initial or Name) Family (Or Last Name)

Inventor's signature Sung Hwa Jung

Date April 19, 2002 Country of Citizenship Korea

Residence Korea, Taejeon-Si KRX

Post Office Address Korea, Taejeon-Si, ulitsa Chungsol,5, kv.1104

Jun _____ Seok _____ PARK _____
(Given Name) (Middle Initial or Name) Family (Or Last Name)

Inventor's signature _____
Date April 19, 2002 _____ Country of Citizenship Korea _____
Residence Korea, Taejeon-Si _____
Post Office Address Korea, Taejeon-Si, ulitsa Sejeon, 103, kv.302 _____

(Given Name) _____ **(Middle Initial or Name)** _____ **Family (Or Last Name)** _____

Inventor's signature _____

Date _____ **Country of Citizenship** _____

Residence _____

Post Office Address _____